

# **Appendix A**



WILEY-VCH

network. Our study of the polymerization kinetics has been aided by some new experimental techniques, which are also described. Crosslinking via both co-polymerization and post-polymerization reactions is covered, and brief mention is made of kinetic modeling as it may apply to superabsorbents.

## 2.1. PREPARATION OF SUPERABSORBENT POLYACRYLATES

Superabsorbent polyacrylates are prepared by free-radical initiated polymerization of acrylic acid and its salts, with a crosslinker, in aqueous solution or as a suspension of drops of aqueous solution in a hydrocarbon. The polymerization chemistry is shown schematically in Figure 2.1. The two principal processes, bulk solution polymerization and suspension polymerization, share many features. The monomer and crosslinker concentrations, the initiator type and concentration, polymerization modifiers, the relative reactivities of the monomers, the basic polymerization kinetics, and the reaction temperature are all significant factors in both processes.

In either process, the monomers are dissolved in water at concentrations of 20–40 wt%, and the polymerization is initiated by free radicals in the aqueous phase. Several types of free-radical sources may be used, including thermally decomposable initiators, redox systems, photochemical initiators, and combinations of them. Redox systems used for the crosslinking copolymerizations include couples of persulfate/bisulfite, persulfate/thiosulfate, persulfate/ascorbate, and hydrogen peroxide/ascorbate. Thermal initiators include persulfates, 2,2'-azobis(2-amidinopropane)-dihydrochloride, and 2,2'-azobis(4-cyanopentanoic acid). Combinations of initiators are used especially when the polymerization takes place over a broad temperature range.

The monomers are polymerized either in the acid form (pH 2–4) or as the par-

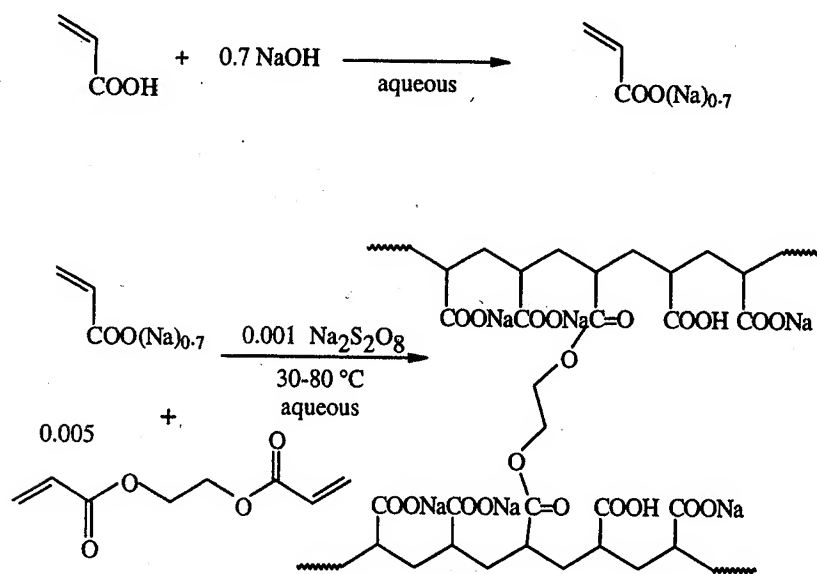
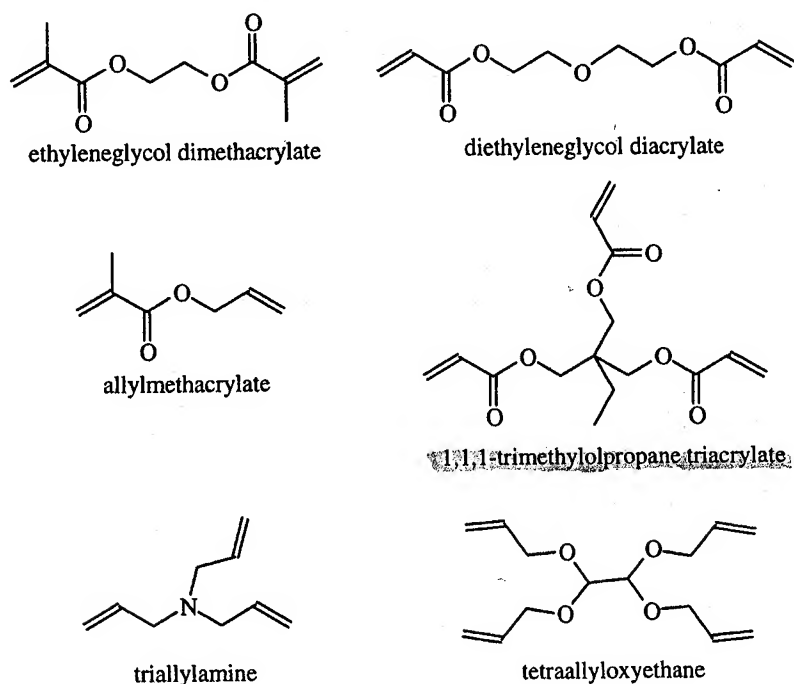


Figure 2.1. Schematic depiction of the chemistry of polymerization of superabsorbent poly(acrylates).

tially neutralized salt (pH 5–7). Inexpensive bases, such as sodium hydroxide and sodium carbonate, are used as neutralizing agents. A choice would be made based on consideration of the pH of the base solution and the resulting potential for hydrolyzing the crosslinker, the solubility limits of the base in water and on the solubility of the monomer salt in water. In suspension polymerizations, the acrylic acid must be neutralized prior to polymerization because of a substantial partition coefficient of acrylic acid in the liquid hydrocarbons used as continuous phase. The polymers made from acrylic acid (and neutralized later) or from the partially neutralized monomer are somewhat different because of the presence or absence of charged monomers and polymers during the formation of the polymer network.<sup>9</sup>

Small amounts of crosslinkers play a major role in modifying the properties of superabsorbent polymers. The co-polymerizable crosslinkers used in superabsorbent polymers range from di-functional compounds, such as diacrylate esters and allylmethacrylate, to tri-functional compounds, such as 1,1,1-trimethylolpropanetriacrylate and triallylamine, and to tetra-functional compounds, such as tetraallyloxyethane. The structures of these substances are shown in Figure 2.2. In addition to modifying the swelling and mechanical properties, the crosslinker affects the amount of soluble polymer formed during the polymerization as a result of its relative reactivity with acrylic acid or sodium acrylate. Efficiency of crosslinking will also depend on steric hindrance and reduced mobility at the site of pendent double bonds, the tendency of a given crosslinker to undergo intermolecular addition reactions (cyclopolymerization), and the solubility of the crosslinker in the monomer mixture. As a result of each of the above variables, a number of polymer-



**Figure 2.2.** The structure of vinyl crosslinkers commonly used in the polymerization of superabsorbent poly(acrylates).

ization additives are also used to ameliorate processing difficulties on a large scale. These additives are not discussed here, because they typically have little effect on the basic chemistry. To describe the synthesis of superabsorbent polymer in a little more detail, two typical synthetic procedures are given below.

### 2.1.1. Example 1: Crosslinking Co-Polymerization of Acrylic Acid

The polymerization reactor is assembled from a 1-L resin reaction kettle, stoppers, polyethylene tubing, and a thermocouple, as shown in Figure 2.3. The reactor contents may be stirred by means of either a magnetic stirrer (3.2-cm PTFE-coated stir bar) or a bladed agitator on a glass or stainless steel shaft. The monomer solution is prepared in the reactor by mixing 250 g acrylic acid, 600 g distilled water, 0.20 g ethylenediaminetetraacetic acid, and 2 g ethylene diacrylate. The monomer solution is agitated and deoxygenated with nitrogen gas bubbled through the solution at a flow rate of  $400 \text{ cm}^3/\text{min}$  for 60 min.

When the requisite deoxygenation time has passed, the initiator solutions are added to the stirred monomer solution, using pipettes or syringes, in the order list-

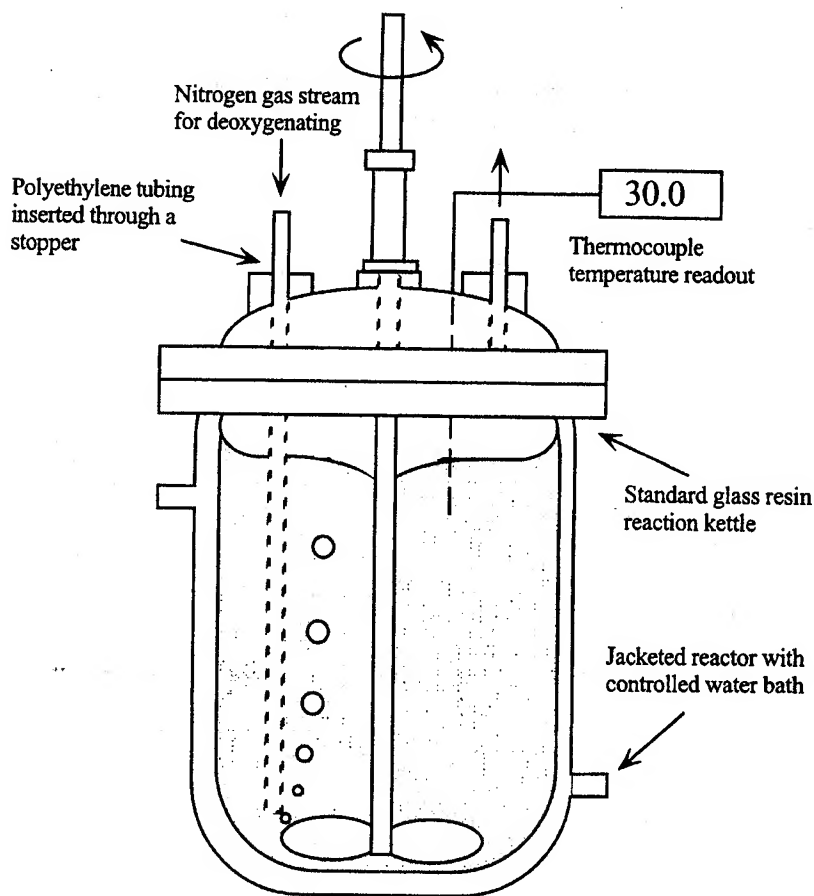


Figure 2.3. Schematic of a reactor suitable for laboratory polymerizations.

# **Appendix B**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Application of: Gerd JONAS et al.  
Serial No.: 10/660,982  
Filed: September 12, 2003  
Confirmation No.: 6109

Examiner: RABAGO, Roberto  
Group Art Unit: 1713

For: **SUPERABSORBENT POLYMER WITH SLOW ABSORPTION TIMES**

Mail Stop AF  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

**AFFIDAVIT UNDER 37 C.F.R. 1.132**

I am Scott Smith, an advisor and manager of the invention described in the present application. I hold a Ph.D. in Organic Chemistry from The University of Cincinnati and specialized in the field of organic synthesis. I started working in the field of superabsorbent polymers in 1989 and continued working in this field to the present. I was employed by Nalco Chemical Company in Naperville, IL from December 1987 to December 1997. My position progressed from Senior Chemist to Group Leader, then Technical Director of Absorbent Chemicals. Since January 1997, I have been employed by Stockhausen, Inc. in Greensboro, North Carolina. My current position is Group Manager of Absorbent Technologies.

I have reviewed the present patent application, the Final Office Action mailed June 29, 2006, and I am aware of the following information regarding examples directed to hydrophilic superabsorbent polymers made using only one neutralization agent. The following Table 1 and the description of the examples C1 to C4 are submitted as comparison to the present invention.

**Table 1**

Example Number	Equilibrium FAUZL Capacity (g/g)	Mean particle size (mm)	Calculated $5+10a^2$ (min)	Calculated $7+10a^2$ (min)	Calculated $10+10a^2$ (min)	Measured Absorption Time (min)	Drop Penetration Value (sec)	Gel Bed Permeability ( $\times 10^{-9} \text{ cm}^2$ )	Floatability (%)
C1	37	0.46	7.1	9.1	12.1	4	<1	79	0
C2	27.5	0.20	5.4	7.4	10.4	3.3			0
C3	33	0.73	10.3	12.3	15.3	6.4			0
C4	34.2	0.45	7.0	9.0	12.0	8.1	<1		100

Superabsorbent polymer compositions identified as Examples C1, C2, C3, and C4 are available from Stockhausen, Inc., Greensboro, NC. Superabsorbent C1 is FAVOR SXM 880, a sodium polyacrylate polymer available from Stockhausen, Inc. that is lightly crosslinked, partially neutralized to a degree of 70mol% with sodium hydroxide.

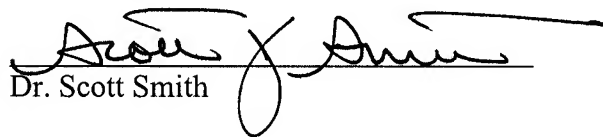
Superabsorbents C2, and C3 are FAVOR SXM 870, a sodium polyacrylate polymer available from Stockhausen, Inc. that is lightly crosslinked, partially neutralized to a degree of 70mol% with sodium hydroxide. Superabsorbent C2 was prepared by sieving a sample of FAVOR SXM 870 and collecting that material which was retained upon a #140 U.S. Standard Sieve but passed through a #50 U.S. Standard Sieve. Superabsorbent C3 was prepared by sieving a sample of FAVOR SXM 870 and collecting that material which was retained upon a #30 U.S. Standard Sieve but passed through a #20 U.S. Standard Sieve.

Superabsorbent C4 is W77553 (P15087), a sodium polyacrylate polymer available from Stockhausen, Inc. that is lightly crosslinked, partially neutralized to a degree of 70mol% with sodium hydroxide.



Table 1, when taken in view of the invention of patent application serial number 10/660,982, shows that the actual absorption times of C1, C2, and C3 do not meet the absorption time of the present invention, and that C4 does not meet the requirement of having a floatability of about 50% or less.

I declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001; and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

  
Dr. Scott Smith

Date: 08/23/06